

5. That the layer affects the position of the Principal Incidence considerably, and also influences the Principal Azimuth.

6. That, consequently, the deduction of the optical constants of a metal from observation of the Principal Incidence and Azimuth alone is liable to considerable error. [In the case of steel this method leads to $\mu = 2.249$ and $\alpha = 3.257$ (see p. 216), while the wider theory yields $\mu = 2.134$ and $\alpha = 2.906$.]

7. That four constants are required to describe the optical properties of a metallic reflector, two of them depending on the nature of the layer of transition.

8. That with these four constants a very satisfactory agreement exists between theory and experiment, as regards both the intensity of the reflected light and the difference of phase between the lights polarised perpendicularly and parallel to the plane of incidence.

The Relation Between the Osmotic Pressure and the Vapour Pressure in a Concentrated Solution.

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(Communicated by W. C. D. Whetham, F.R.S. Received November 11, 1905 ; received in Revised form January 3,—Read January 25, 1906.)

1. The relation between the vapour pressure and the osmotic pressure of a solution is often investigated by considering the equilibrium of a column of solution separated at the bottom from the pure solvent by a semi-permeable membrane, and placed in an atmosphere of vapour from the solvent. Now the hydrostatic equilibrium of the vapour column gives

$$\delta p = g s^{-1} \delta h,$$

where p is the vapour pressure of the pure solvent, g the acceleration due to gravity, h the height above the surface of the pure solvent, and s the specific volume of the vapour. Hence considering the equilibrium of the liquid column we get

$$P + p - p' = \rho \int_{p'}^p s dp,$$

when P is the osmotic pressure, p' the vapour pressure of the solution, p that of the pure solvent, and where ρ is the effective mean density of the column of liquid.

The writer was led to doubt whether this method could be applied to concentrated solutions, by the fact that a different result is obtained when the same problem is attacked by the consideration of an isothermal cycle in accordance with Van't Hoff's method. This method, when fully worked out, seems to lead to the equation :—

$$Pv_s + pv_s - p'v_s' + W - c \frac{dW}{dc} = \int_{p'}^p s dp,$$

where P, p, p' and s have their previous meanings, v_s is the increment in volume of a large mass of solution at a hydrostatic pressure $P+p$ when unit mass of solvent is added, v_s' the increment in volume of a large mass of solution at a hydrostatic pressure p' when unit mass of solvent is added, W is the work done in compressing unit mass of solution from a hydrostatic pressure p' to a hydrostatic pressure $P+p$, and c is the concentration measured by the mass of solute in unit mass of solution.

In considering the discrepancy between these two results the writer had come independently to the same conclusion as the Earl of Berkeley and Mr. Hartley, namely, that in the column method error is introduced through neglect of variation, owing to the action of gravity, of the concentration at different levels. As however the writer's conclusions differ, in some possible cases notably, from theirs, the following investigation is submitted.

2. In the column method what is undoubtedly found is a perfectly rigid result connecting the osmotic pressure corresponding to the concentration at the bottom of the column and the lowering of vapour pressure corresponding to the concentration at the top. In order therefore to apply the result to a comparison of the osmotic pressure and vapour pressure of solutions at the same concentrations, it becomes necessary to obtain and employ a correction that will give the osmotic pressure corresponding to the concentration at the top in terms of the known osmotic pressure corresponding to the concentration at the bottom. It is to be noted that in all cases osmotic pressures must be computed for equilibrium between solution and pure solvent under one definite pressure, say that of the vapour, for, as Duhem has pointed out,* the osmotic pressure of a solution, defined as the difference in the hydrostatic pressures of solution and solvent when in equilibrium through a semi-permeable membrane, is a function not only of the concentration of the solution but also of the hydrostatic pressure of the solvent. Occasion will arise to return to this point, since, as will be shown, on it depends the discrepancy between the results of the Earl of Berkeley and Mr. Hartley and of the writer.

* 'Mécanique Chimique,' vol. 3, p. 64.

A thermodynamic argument which seems to satisfy these considerations is as follows: Consider a column of solution of such height as to be in equilibrium with pure solvent through a semi-permeable membrane at its base, and further suppose a large flat reservoir at the level of the summit and filled with solution at the concentration of the solution there. Let the following isothermal reversible cycle be performed:—

Let the top of the column of solution be covered with a piston which exerts on the solution a hydrostatic pressure equal to the vapour pressure. Let the semi-permeable membrane also be part of a piston, and the pure solvent be covered by a piston exerting on it a pressure equal to its vapour pressure. Suppose all the pistons to be weightless.

Then (1) keeping the piston covering the solution fixed, move the piston separating solution and solvent so as to remove δm of solvent from the solution, the piston covering solvent being free to move. Then work done by the system is $-\{P_1 D - p(u - D)\} \delta m$, where P_1 is the osmotic pressure corresponding to the concentration at the bottom of the column, $D\delta m$ is the loss in volume of the column, p is the vapour pressure, and u the specific volume of the solvent. The operation being infinitely slow, the solvent will be drawn from throughout the solution and the process will be reversible.

(2) Cover the semi-permeable membrane between solution and solvent by a shutter; then connect the reservoir at the top with the column through a semi-permeable membrane. Further, let the reservoir be closed by a piston exerting on the solution in it a pressure equal to its vapour pressure. Now, since the volume of the columns may be as large as is desired, we may neglect variation of the concentrations due to the above-described loss of δm of solvent, and therefore the solution at the top of the column and in the reservoir may be taken as still at the same concentration. Hence, if the piston at base of column be fixed, that at top be free to move and that between top and reservoir be moved so as to transfer δm of solvent from reservoir to column, there is no osmotic work, and work done by the system $= \delta m p' (D - v_s')$, where p' is the vapour pressure of solution at top of column or in reservoir, and v_s' is the increment in volume of solution at that concentration, and at a pressure p' on adding unit mass of solvent to a large amount of solution.

(3) Disconnect the reservoir from the column and compress the solution in the reservoir to a pressure $P_2 + p$, where P_2 is the osmotic pressure for the solution in the reservoir (since this may be of any size, P_2 is also the osmotic pressure corresponding to the concentration at the top of the column). The work done by the system is $-MW$, where M is mass of solution in the

reservoir, and W the work done in compressing unit mass from a pressure p' to a pressure $P_2 + p$.

(4) Connect the reservoir through a semi-permeable piston with pure solvent, and by moving piston introduce δm of solvent into reservoir. The pure solvent is supposed to be covered by a piston exerting on it a hydrostatic pressure equal to its vapour pressure, and the work done by the system will thus be $[P_2 v_s - p(u - v_s)] \delta m$, where v_s differs from v_s' in being for solution at a pressure $P_2 + p$ and not p' .

(5) Lower the column of solution through a height $D\delta m/a$, where a is the sectional area of the column, and raise a mass δm of solvent through the height h where h is the height of the column. The work done by the system is equal to the loss in energy of position, that is $hga D\delta m/a - hg\delta m$ or $-hg(1 - \rho D)\delta m$ where ρ is the effective mean density of the column. But $hg\rho = P_1 + p - p'$, since that is the condition for equilibrium across a semi-permeable membrane at the foot of the column. Hence the work is $-(1 - \rho D)(P_1 + p - p')\rho^{-1}\delta m$.

(6) Release the pressure on the solution in the reservoir to p' , then work done by the system is $+ \{MW + \delta m \cdot d/dm(MW)\}$ where m is mass of solvent, that is $+ \{MW + W\delta m - \delta mcdW/dc\}$, c being as before mass of solute in unit mass of solution.

The above is a complete cycle in all essentials, and being isothermal and reversible we may collect the work and equate to zero. Hence

$$0 = -[P_1 D - p(u - D)]\delta m + \delta mp'(D - v_s') - MW + [P_2 v_s - p(u - v_s)]\delta m - (1 - \rho D)(P_1 + p - p')\{\rho^{-1}\delta m + MW + W\delta m - \delta mcdW/dc\},$$

whence

$$(P_1 + p - p')\rho^{-1} = (P_2 + p)v_s - p'v_s' + W - cdw/dc.$$

Hence, if there be a column of solution whose top surface is under a pressure equal to the vapour pressure, and which is in equilibrium at its base, through a semi-permeable membrane, with pure solvent (at a pressure equal to its vapour pressure), this equation gives the connection between the osmotic pressures, corresponding to solution at the top and bottom of the column, computed in each case with reference to solvent under the pressure of its vapour.

Such a column is identical with that used in deducing the relation between osmotic pressure and vapour pressure, and we have

$$P_1 + p - p' = hg\rho = \rho \int_p^p sdp,$$

on substituting from the above,

$$(P_2 + p)v_s - p'v_s' + W - c \frac{dW}{dc} = \int_p^p sdp,$$

which is identical with the result previously quoted as obtainable by Van't Hoff's method.

Since $v_s - v_s'$ is in general very small as also W and cdW/dc , and since $p - p'$ is negligible compared with P , the result reduces to the approximate equation

$$Pv_s = \int_{p'}^p s dp,$$

or assuming Boyle's law to hold for the vapour,

$$Pv_s = sp \log p/p'.$$

3. The result deduced by Lord Berkeley and Mr. Hartley is

$$Pu = sp \log p/p',$$

where u is the specific volume of the solvent.

Since v_s is the increment in volume of a large mass of solution when unit mass of the solvent is added, these equations will only be identical when this increment is equal to the volume of solvent added, that is when the contraction on dilution is negligible.

In many cases, *e.g.*, cane sugar dissolved in water, this will be the case up to considerable concentrations, but in other cases it will not be so; thus in solutions of caustic soda in water v_s and u differ appreciably at comparatively moderate concentrations, and the difference rises to 14 per cent. in a 50-per-cent. solution.* *If, therefore, the relation between osmotic pressure and vapour pressure is to be applied in the case of concentrated solutions, it is necessary to determine v_s , and if v_s differs appreciably from u , to employ v_s and not u .*

4. As has already been stated, the presence of u for v_s in the equation due to Lord Berkeley and Mr. Hartley depends on the assumption that the osmotic pressure (*i.e.*, the difference in hydrostatic pressure between solution and solvent when in osmotic equilibrium) is independent of the hydrostatic pressure of the solvent and, for example, would not change if the whole system was compressed in a hydrostatic press.

In order to show that the removal of this assumption leads to the writer's

* The following figures are based on a table published ('Phil. Trans,' Series A, vol. 204, p. 273) by Mr. W. R. Bousfield and Dr. Lowry for a solution at 18° C. :—

Percentage NaOH.	v_s .	Percentage NaOH.	v_s .
5	0.9979	30	0.9333
10	0.9908	35	0.9120
15	0.9804	40	0.8998
20	0.9671	45	0.8724
25	0.9524	50	0.8585

The specific volume of water at 18° was 1.00134.

result it is necessary to obtain an equation for the variation in osmotic pressure when solution of constant concentration is successively in equilibrium with solvent at two different hydrostatic pressures. This relation can be obtained as follows by considering an isothermal reversible cycle performed on a system, consisting of a large mass of solution, connected through a semi-permeable piston with a large mass of solvent. Suppose solution and solvent to be confined by pistons through which pressures can be applied.

(1) Apply to the solvent a pressure π_1 and such a pressure to the solution as will give osmotic equilibrium. Let this pressure be $P_1 + \pi_1$, so that P_1 is the osmotic pressure. Then the work done by the system, if the piston confining the solution be kept stationary and that between solution and solvent moved so as to introduce a mass δm of solvent into the solution, is $[P_1 v_{s1} - \pi_1(u_1 - v_{s1})] \delta m$, when u_1 is the specific volume of the solvent at a pressure π_1 and v_{s1} is the increment in volume of a large mass of solution at a pressure $P_1 + \pi_1$ on the addition of unit mass of solvent.

(2) Compress the solvent to a pressure π_2 , simultaneously compressing the solution in such a way as to maintain osmotic equilibrium. Let $P_2 + \pi_2$ be the final hydrostatic pressure of the solution, so that P_2 is then the osmotic pressure when the solvent pressure is π_2 . If W be the work done in compressing unit mass of solution from $P_1 + \pi_1$ to $P_2 + \pi_2$, M being the mass of solution, W' the work done in compressing unit mass of solvent from π_1 to π_2 , and M' the mass of the solvent. Work done by the system $-(MW + M'W')$.

(3) Move the semi-permeable piston so as to remove a mass δm of solvent from the solution, keeping stationary the piston confining the solution. The work done by the system is $[-P_2 v_{s2} + \pi_2(u_2 - v_{s2})] \delta m$, where u_2 is the specific volume of the solvent at a pressure π_2 , v_{s2} is the increment in volume of a large mass of solution at a pressure $\pi_2 + P_2$ when unit mass of solvent is added.

(4) Release pressure on solvent to π , releasing that on solution so as to maintain equilibrium. The work done by the system is equal to

$$\left(MW - \delta m \frac{d(MW)}{dm} + M'W' + \delta m W' \right), \text{ or } MW + M'W' + \delta m \left(W' - W + c \frac{dW}{dc} \right).$$

The above is a complete isothermal reversible cycle.

Collecting the terms for the work and equating to zero we have

$$0 = [P_1 v_{s1} - \pi_1(u_1 - v_{s1})] \delta m - MW - M'W' \\ - [P_2 v_{s2} - \pi_2(u_2 - v_{s2})] \delta m + MW + M'W' + \delta m (W' - W + c dW/dc),$$

whence

$$P_2 v_{s2} - \pi_2(u_2 - v_{s2}) = P_1 v_{s1} - \pi_1(u_1 - v_{s1}) + W' - W + c dW/dc.$$

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Since in general, $W' - W + cdW/dc$, $v_{s2} - v_{s1}$, $u_2 - u_1$, will be quite negligible, we may neglect change of volume due to compression and write

$$(P_2 - P_1) v_s = (\pi_2 - \pi_1) (u - v_s) \quad \text{or} \quad \frac{dP}{d\pi} = \frac{u}{v_s} - 1.$$

Now in the deduction, due to Lord Berkeley and Mr. Hartley, of the variation of the osmotic pressures corresponding to the concentrations at different levels in a column of solution, it is shown that if P' be the osmotic pressure when solution at the top of a column is connected through a semi-permeable membrane with solvent at a pressure p (that of its vapour), and if P be the osmotic pressure when solution at the bottom of the column (height h) is in equilibrium with solvent at a pressure $p + \rho_0 gh$, where ρ_0 is density of the solvent,

$$P - P' = (\rho - \rho_0) gh,$$

where ρ is the mean density of the column of solution. Let P_0 be the value to which P would change if the solvent pressure changed from $p + \rho_0 gh$ to p , then $P - P_0 = \rho_0 gh (u/v_s - 1)$, or subtracting from the last equation and remembering that ρ_0 is equal to u^{-1} , we get

$$P_0 - P' = (\rho - v_s^{-1}) gh.$$

But to the required degree of accuracy we have from the column method discussed by Lord Berkeley and Mr. Hartley,

$$P_0 = \rho gh = \rho sp \log p/p',$$

where P_0 is the osmotic pressure corresponding to a solution at the bottom of the column and a solvent pressure p , ρ is the mean density of the column, h its height, $p - p'$ the lowering of vapour pressure for solution at the top.

Hence if P be the osmotic pressure corresponding to this solution at the top (and a solvent pressure p),

$$P_0 - P = \rho gh - v_s^{-1} gh;$$

or, subtracting from the last equation,

$$P = v_s^{-1} gh \quad \text{or} \quad P v_s = sp \log p/p',$$

which is the writer's result.

In conclusion, I have to thank Mr. Whetham for very valuable criticism.